Experimental report

15/09/2016

Proposal:	**7-05-461**	**Council:**	4/2016
Title:	Understanding the Grafting of fluorescent molecules on double-walled carbon nanotubes.		
Research area:	Materials		

This proposal is a new proposal

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Samples:
FITC
Streptocyanine
Diamine-FITC
DWNT @ FITC
DWNT-doubleOx
DWNT-diamine-Streptocyanine
1,4-diaminobutane
Diamine-streptocyanine
DWNT-diamine-FITC
DWNT @ Streptocyanine
DWNT-diamine

Instrument	Requested days	Allocated days	From	To
IN1 LAG	7	7	30/05/2016	06/06/2016

Abstract:

In the fields of nanotoxicology and biomedical applications of carbon nanotubes (CNTs), it is often required to graft fluorophores on their surface in order to track them inside cells. For covalent grafting, the question of the competition between real grafting and simple adsorption is very relevant and has never been investigated rigorously. However, fundamental questions are raised as there is no simple evidence that a fluorophore adsorbed on a CNT will stay there forever once inside a cell (molecules with a stronger affinity could lead to desorption of the fluorophore), leading to wrong conclusions. These questions have already been investigated in a previous PhD Thesis using different techniques (Raman, IR, etc.) but none of them were able provide clear answers. On the contrary, in this PhD project the use of inelastic neutron scattering spectroscopy has already showed a strong ability to bring essential information that allowed us to have a better understanding of the grafting mechanisms. In order to go further and finally obtain the answers we aim, we need now to quantify precisely these mechanisms.

The CIRIMAT is working on the Catalytic Chemical Vapour Deposition (CCVD) synthesis of carbon nanotubes (CNTs) for more than 15 years and its expertise in this field is acknowledged at the international level, in particular in relation with double-walled CNTs (DWNTs) and the toxicity of the DWNTs.

The aim of this experiment, which is on the framework of an ILL PhD project, is to characterize (covalent or non-covalent) the interaction between CNTs and model molecules (fluorophores), aiming at answering the following fundamental questions:

(i) What are the adsorption sites in CNTs samples (different surface sites are available)?
(ii) What is the ratio between covalent and adsorbed molecules in the case of a covalent grafting?

Seven different samples were chosen for this experiment (figure 1). Three of them were references samples, corresponding to the two different molecules used during the functionalization (1 & 3). While sample 2 is the product of reaction between samples 1 and 3 and acts as a witness of the covalent bonding of the latter ones. This type of bond is looked for in this experiment.

The other samples were synthetized in the CIRIMAT Toulouse. Sample 4, 5 and 6 correspond to three different steps of the functionalization process of Double-walled carbon nanotubes (DWCNTs). The first one was constituted of double-oxidized DWCNTs (4), the second one was DWCNTs with grafted putrescine (1,4-diaminobutane) (5) and the third one, which corresponds to the final step of the functionalization process was made of DWCNTs-putrescine with grafted Fluorescein Isothiocyanate (FITC) (6). Finally, sample 7 is constituted by DWNTs with adsorbed FITC and acts as a witness for the non-covalent grafting of the FITC.

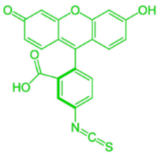
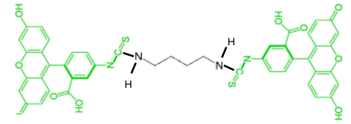
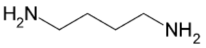
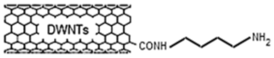
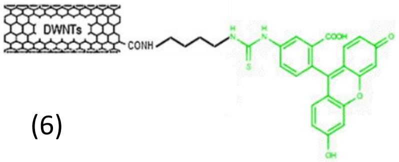
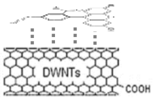
	 (1)	 (2)	 (3)
 (4)	 (5)	 (6)	 (7)

Figure 1: Representation of the seven measured samples

This experiment has been performed on IN1-LAGRANGE, using the Cu331 monochromator, increasing the analysis time and focusing on the stretching vibrational range. It allowed us to improve the statistics as well as the energy resolution in the stretching region of the INS spectra (see figure 2). Indeed, this region contains very interesting information about the characteristic vibrational bands of the covalent grafting occurring in between sample (5) and (6). Unfortunately, in this configuration the neutron flux is divided by three and forced us to choose the seven samples above over the eleven originally planned in order to remain on time with the spectrometer schedule.

Nevertheless, the well-defined spectra obtained in this experiment (see figures 3 & 4) are the key to ensure a precise quantification of the functionalization process efficiency and, therefore, are the key to answer the central questions mentioned above.

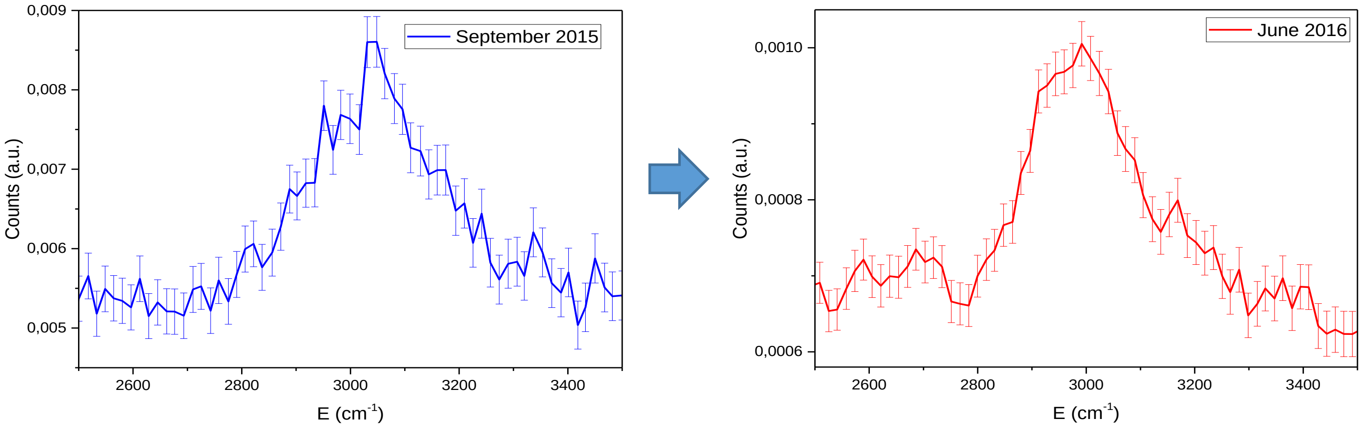


Figure 2: Illustration of the spectrum quality improvement for the stretching region of sample 6

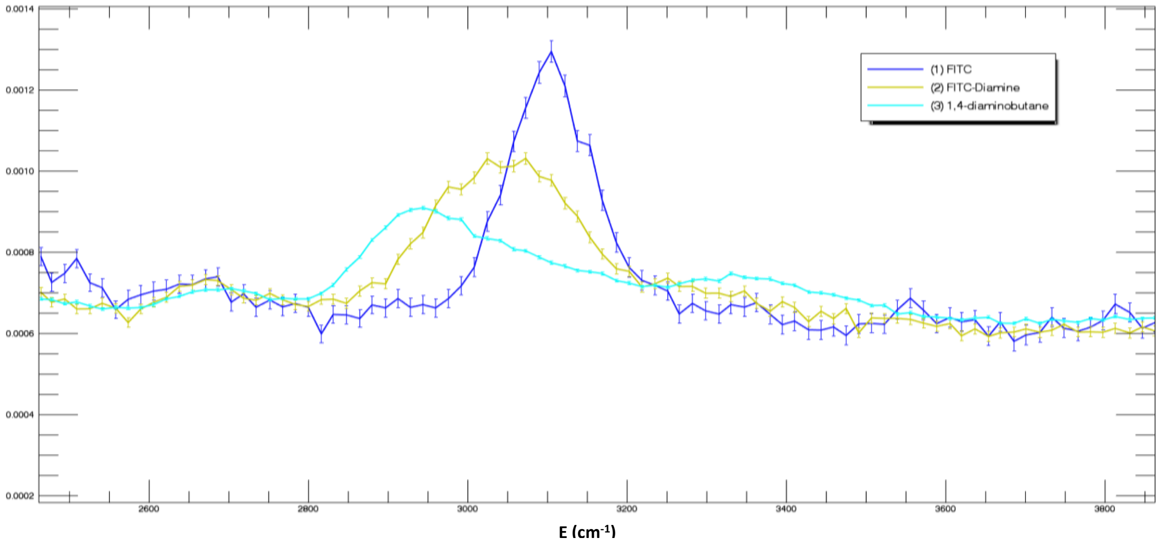


Figure 3: Normalized INS Spectra of the references samples

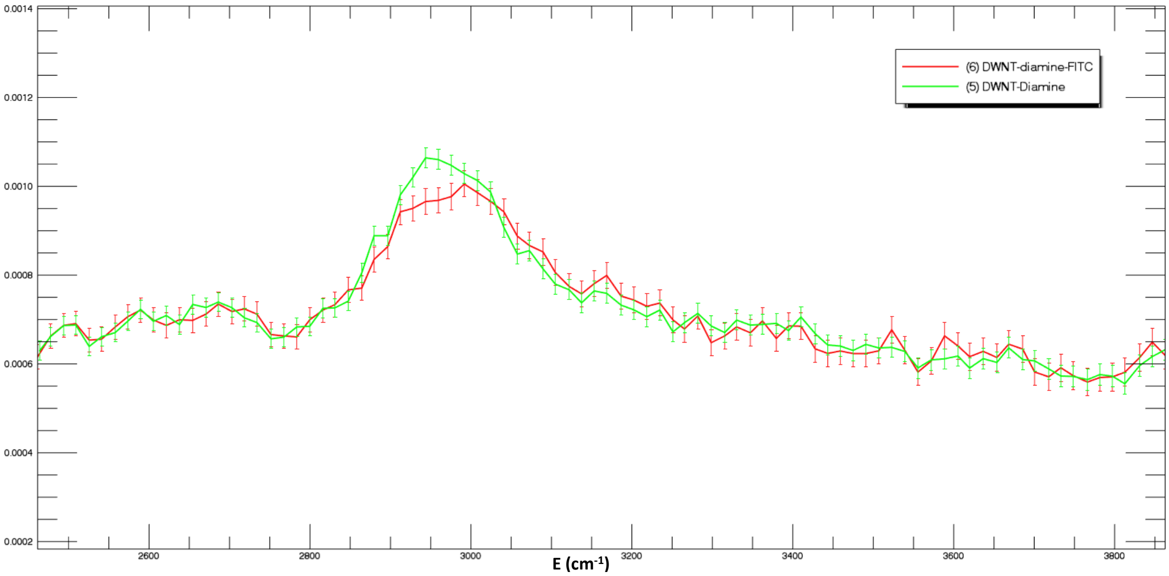


Figure 4: Normalized INS spectra of the main DWNTs samples